STUDIES ON THE LEACHING SYSTEMS OF SOME VEGETABLE TANNING MATERIALS

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LEACHING of vegetable tanning materials is practised by Indian tanners by blending different tan materials (hydrolysable and condensed) together for a long time. In some parts of India the blending of tanning materials is generally done only with babul and myrab and in some other parts the blending is practised with mangrove, babul and myrab or wattle, babul and myrab, etc. The blended liquors are prepared by countercurrent technique with the usual tannery water in 8-10 days time. But it is known that the solubility of hydrolysable tannins with water is much more than that of condensed tannins, as the former being ester type of tannin are less agglomerated and easily become soluble. The enhanced solubility is also due to more of hydroxyl groups in the hydrolysable tannins. But the condensed tannins which remain in highly aggregated form and having less of hydroxyl groups are slowly soluble in water. Recent work has shown that infusions of myrab[1] and babul[2] if exposed to atmosphere for about a week, about 40% and 20% of tannins respectively are precipitated out in the form of sludge. It has also been noticed that if the barks of typical condensed tannin like mangrove are dried considerably, the tan content of the bark gets reduced considerably. If the barks are crushed properly the extraction of some of the condensed tannins becomes easier

The present work is designed to show the merits and demerits of present leaching systems and how best these could be improved.

Experimental

Four different sets of experiment were conducted namely: 1. Individual leaching of different tanning materials namely myrab, babul, mangrove (goran) and wattle. 2. Blended leaching of babul and myrab and mangrove (goran) and myrab. 3. Individual leaching of myrab in 12 hours. 4. Individual leaching of myrab, babul and goran and then blending.

1. *Individual leaching of different tanning materials*

Three different sets of experiment were conducted as follows:

(a) 100 gm. of different tanning materials namely myrab, babul, goran and wattle (all in dried condition) after crushing in almost powder form ($\frac{1}{2}$" mesh size) were soaked separately with 400 ml. of water (30°C) for 12 hours, after which the leached infusions were filtered. The volume of the filtrates of each was recorded and the same volume of water was again poured in the respective tanning materials and kept 12 hours more in the similar way. The leached infusions were again filtered. In this way the different tanning materials were extracted 4 more times. In the similar way, in another set of experiment the tanning materials were leached first 4 times with cold water (30°C) and last 2 leachings with boiling water (the water was only boiled and poured on the tanning materials).

(b) In another set of experiment the different tanning materials were taken in the similar way as are generally taken in commercial tannery viz: 1" x $\frac{1}{4}$" in the case of babul, wattle and goran and in the case of myrobalan nuts, breaking them into two), without reducing the size of the tanning materials considerably. Other procedures are the same as before.

(c) In the third set of experiment, e crushed myrab and babul were ached separately with water at 10°C. The extraction procedure remained the same as before. Only difference being the leached infusions were collected after every 24 hrs. instead of 12 hrs. for 6 days.

The total solubles of the liquors of each extraction were then determined. The spent barks and nuts were also analysed. The results are given in table I.

2. *Blended leachings of babul and byrab and mangrove and myrab.*

Here also two sets of experiment were conducted:

(a) Blends of finely crushed tanning materials ($\frac{1}{2}$" mesh size) of babul (60 gm.) and myrab (20 gm), goran (50 gm.) and myrab (25 gm.) were made. Four times of water were then added in each blend. Other procedures are the same as in No. 1.

(b) Similar experiment with lightly crushed tanning materials (1" x $\frac{1}{4}$" in the case of babul, wattle and goran and in the case of myrobalan nuts, breaking them into two) was conducted.

3. *Individual leaching of myrab in 12, hours*

100 gm. of crushed myrab nuts were leached successively for 6 times after every 2 hours in the same way as described in No. 1. The successive leachings were then mixed and analysed. The spent nuts were also analysed.

4. *Individual leaching of myrab, babul and goran and then blending*

A countercufrent leaching of myrab, babul and goran was made by using 100 gm. of each of the tanning materials and starting with 400 ml. water at room temperature followed by successive leaching with 250 ml. water. The liquors were transferred to the next beakers after every 12 hours. In this way after the 6th countercurrent leaching all the liquors were collected and kept separately. In another experiment myrab nuts were extracted in 6 countercurrent leachings in 12 hours. Babul, myrab and mangrove myrab were then mixed on total soluble basis in the ratio 2:1 and 1:1 respectively. All the results are given in the table.

Discussion of results

The result showed that when lightly crushed (commercial quality) and very finely crushed myrab nuts are extracted with water at room temperature (30°C) about the same quantity of water solubles (*Ca* 50%) are extracted in the first leaching in both the cases. In the subsequent leachings almost the same quantity of water solubles were extracted in both the cases. In the first three leachings about 77% of total water solubles were leached in both the cases. Another about 13% of total water solubles were extracted in the next three leachings. Rest of water solubles could not be extracted in 6 cold water leachings. This indicates that myrab tannins, which are typical hydrolysable type of tannin, can easily be extracted almost completely (*Ca* 90%) from even lightly crushed nut (commercial quality) with cold water.

But when other tanning materials like babul, goran and wattle were not crushed properly, the water solubles were found to be negligible as compared to myrab. In the first leaching 24.6%, 15.8% and 10% of the total water solubles were extracted from babul, mangrove and wattle respectively. In the 2nd and 3rd leaching about 4-12% of total water solubles were extracted in each leaching from these barks. About 20-50% of total solubles were extracted from babul, goran and wattle in the first 3 leachings, the extraction from wattle being minimum (*Ca* 20%) followed by goran (*Ca* 30%) and babul (*Ca* 42.4%). In the 4th and 5th leaching the solubility of all the tanning materials namely myrab, babul, goran and wattle (both crushed and uncrushed) were found to be almost the same. In the 6th leaching the solubility of all the condensed tanning materials (both crushed and uncrushed) was found to be more than myrab, which was adready almost free of water solubles. After 6 leachings the total solubles extracted from lightly crushed (commercial quality) tanning materials were found to be as follows: Myrab — 90.4%; Babul — 56.4%; Goran — 47%; Wattle — 37%.

These figures indicate that if the condensed tanning materials are not properly crushed, the total water solubles extracted even in 6 leachings in the case of goran and wattle are less than water solubles extracted in the first leaching of myrab. But in the case of babul it is about 7% more than first leaching of myrab.

But when the condensed tanning materials are finely crushed, the water solubles of both babul and wattle were about 32% in the first leaching i.e. about 16% less than the water solubles of myrab in the first leaching. But in the case of goran it is almost the same (*Ca* 15%) as the uncrushed one. This indicates that by crushing the dried barks of wattle and babul, the water solubles could be considerably increased but not so in the case of dried. In the 2nd leaching the efficiency of goran extraction of babul is still retained (*Ca* 26%) but not in the case of wattle (*Ca* 14%). But in the case of goran it is almost the same as in first leaching. In the first 3 leachings the total quantity of water solubles of crushed babul, mangrove and wattle were about 70%, 39% and 56% respectively.

As has alredy been mentioned before, that in the 4th and 5th leaching the solubility of all the tanning materials (both crushed and uncrushed) remained almost the same and in the 6th leaching, as in uncrushed materials, the solubility of all the condensed tanning materials was found to be more than myrab. After 6 leachings the total solubles extracted from fully crushed tanning materialls were found to be as follows; Myrab — 91.4%; Babul — 81.6%; Goran — 56.4%; Wattle — 70.2%.

But when the last two leachings are conducted with boiling water (water was only boiled and poured on the tanning materials) about 8% more of water solubles was found to have been extracted. But to extract most of the tannins, continuous boiling water is necessary in the last 2-3 leachings.

This indicates that water solubles of crushed babul and wattle can be considerably increased even when extracted with cold water (30°C). But in the case of dried goran the water solubles can be extracted to a slightly higher quantity when it is in the powdered form. To extract the total quantity of tannin the last 2-3 leachings must be conducted with boiling water. But it has been observed that when mangrove barks are dried to a considerable extent it is not possible to extract a majon portion of tannins. So, this bark should be extracted in almost fresh condition after chipping to a considerable extent (*Ca* ½" mesh size)

The solubility of bauul tannin was found to be very high when the bark was crushed to ½" mesh size. Presumably, leucocyanidin gallate i.e. gallic acid esterified with flavonoid compound, which is the main constituent making the babul tannin might be responsible for the easy solubility of the babul tannin. Babul bark was also found to contain chebulinic acid, gallic acid and high sugar content, which are common in hydrolysable tanning materials. Babul tannins can therefore be called samihydrolysable tannin, as hydrolysable tannins contain tannins having mainly gallic acid esterified with glucose. Like hydrolysable tannin (myrab), babul was found to lose tannin due to hydrolysis of leucocyanidin gallate. Like myrab, babul should also be extracted in minimum possible time.

Wattle tannins do not contain any gallic acid either in esterified form or in free state. These tannins are mainly based on leucofisetinidin 7,3', 4'-flavan-3,4-diol) and leucorobinetinidin (7,3'4',5'-flavan-3,4-diol), the latter predominating. The galloyl group in the (B) ring of the flavonoid compound (leucorobinetinidin) of wattle tannins is presumably responsible for the more solubility of the tannins when the bark is in the finely crushed condition.

From the above experiment, it is evident that if the bark of the condensed tanning materials is not properly crushed, water cannot go deep inside the dried fibres of the materials and solubilise most of the tannins in 6-8 leachings. Most of the tannins, therefore, left in the blended exhausted tanning materials in the commercial tannery are presumably from condensed tanning materials, as it has been observed in the present work that most of the tannins (*Ca* 90%) from hydrolysable tanning materials (crushed or uncrushed myrab) can easily be extrac-

ted with cold water (30°C) in 6 leachings. If the condensed tanning materials are not crushed with the crushing machine to about ½" mesh size, hot water leaching cannot improve considerably the efficiency of extraction.

In the experiment where the leaching of crushed babul and myrab was conducted with water at 10°C, it was observed that in the first leaching, about 23% of total water solubles of myrab and 15% of babul were extracted i.e. about ½ the quantity extracted with water at 30°C in the first leaching. In the 2nd leaching the extraction of water solubles from myrab and babul was 11.4% and 7% respectively i.e. much less than the water solubles extracted with water at 30°C. Even in 9 leachings, only about 62% of total water solubles from myrab and 40% from babul were extracted.

This experiment thus showed that even when the tanning materials are properly crushed, the water solubles of both hydrolysable and condensed tanning materials can be extracted only partially (*Ca* 50-60%) during winter season, when the temperature of some parts of India comes down between 1-10°C.

The results also indicated that it is not possible to maintain the ratio of water solubles of the final product of blended hydrolysable and condensed tanning materials even partially, if the latter are not finely crushed. Even if the dried condensed tanning materials like mangrove and wattle are crushed it is not possible to leach out most of the tannins with cold water in 6-8 leachings. To make an efficient extraction of tannins hot water is absolutely necessary. In blended tanning materials, as are generally used in India, the ratio of water solubles of the final product would be different in almost every lot.

In the experiment where the tan materials are first blended and then extracted, the resultant water solubles were found to retain the clarity of the solution more than if separately extracted and blended. In the former case, sludge formation was found to be slightly less than the latter ones. Presumably, in the blended leaching some of the hydrolysable tannins which are likely to be precipitated out are kept in solution for some time by the condensed tannins due to mutual solubilisation, making the resultant liquor clearer.

From the experiment on leaching of myrab in 12 hours, it was observed that most of the tannins from myrab (uncrushed and crushed) can be extracted with cold water in 12 hours. In the experiment when myrab nuts were leached in countercurrent technique in 6 leach pit system in 12 hours and 3 days, and from the final product of these two liquors when analysed, it was observed that the one which was extracted in 12 hours yielded more tannin than the one which was extracted in 3 days. If heat is applied this can be leached even in 6 hours. The extraction of myrab tannin should therefore be conducted in minimum possible time (8-12 hrs.) with cold and hot leachings.

In the experiment when myrab, babul, wattle and goran are extracted with water at room temperature separately in 12 hours (myrab) and 3 days (other tanning materials) in 6 leach pit system and then blended, there is no problem of maintaining the ratio of water solubles of these two types of tannins. Immediately after mixing the liquor, tanning should be started to avoid greater sludge formation.

In most of the tanneries of India, where babul and myrab are blended without crushing the former properly, and extracted in countercurrent technique with water at room temperature in 8-10 leach pit system, at least 25-30% and 40-50% of total water solubles are found to be wasted during summer and winter seasons respectively, in the tanning materials of the exhausted pits. The present experiments have showed that these are mainly from babul bark during summer and from both during winter. At another at least 12-15% of water solubles are wasted in the form of sludge due to hydrolysis, during long leaching.

This figure showed that out of one tonne of babul bark used for leaching at least 1/3rd tonne is wasted or in other words a tannery which consumes 300 tonnes of babul bark yearly would lose as much as Rs. 20,000/- for bark alone, if the price of the babul bark is about Rs. 200/tonne. And during winter (about 4 months), about 30% of myrab tannin is wasted, i.e. a tannery consuming 300 tonnes of myrabnuts annually would lose about Rs. 3,000/- for nuts only, if the price of the same is about Rs. 100/ tonne.

In India, about 1,50,000 tonnes of babul bark are produced annually, of which about 40-50,000 tonnes of tanning material can be considered wasted due to an improper leaching system. This waste tanning material can easily yield about 8-10,000 tonnes of extract, showing thereby that the import of wattle extract can be reduced to a considerable extent.

But this wastage of tanning materials can easily be prevented if they are properly crushed with the crushing machine before leaching and making the last 2-3 leachings with hot water (80°C) by maintaining the temperature of water with the help of steam. So, the tanneries which are leaching the tanning materials should be equipped with bark crushing machine and boiler.

The following points are, therefore, suggested for making a very efficient leaching of two different types of tanning materials, which are generally used in the tannery, without disturbing the existing system: (1) The condensed tanning materials, particularly mangroves, should not be allowed to dry too much and should be crushed with the crushing machine. (2) The blended leaching of hydrolysable and condensed tanning materials should be completed within 2-3 days' time, depending on the type of the condensed tanning materials used, in 6 leach pit system (in the case of a blend of myrab and babul, the first 3 leachings should be conducted with the usual tannery water in 1½ days and the last 3 leachings with water at 80°C in 1½ days). (3) Hot water (80°C) must be used in the last 3 leachings in order to extract most of the tannins. The temperature of water should be maintained with the help of steam. (4) The tanneries which are situated in remote villages, where there is no electric current to run the crushing machine, should buy crushed bark from the places, where crushed material would be available.

To confirm the efficiency of the suggested leaching system, a pilot plant experiment was conducted in the leach yard with a blend of babul and myrab (3:1) and the results were found to be very promising. Spent tan contained on 10% moisture basis, 1.1% water solubles, 0.45% tannin and 0.65% nontaan.

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TABLE I

LEACHING OF TANNING MATERIALS (UNCRUSHED COMMERCIAL SAMPLES) WITH COLD WATER

a = % water solubles : b = % of 'a' on total leachables

Leach No.		Myrab	Babul	Goran	Wattle	Babul + myrab 3 : 1	Goran + myrab 2 : 1
	a	24.8	5.7	3.8	3.5	10.4	10.9
I							
	b	49.6	24.6	15.8	10.0		
	a	7.7	2.4	1.7	1.4	3.7	3.2
II							
	b	15.4	10.4	7.0	4.0		
	a	6.2	1.7	2.0	2.2	2.6	2.6
III							
	b	12.4	7.4	8.3	6.4		
	a	2.5	1.0	1.1	1.1	1.3	1.3
IV							
	b	5.0	4.4	4.5	3.2		
	a	2.2	1.1	1.3	1.9	1.2	1.4
V							
	b	4.8	4.6	5.5	5.4		
	a	1.4	1.2	1.2	2.8	1.10	1.4
VI							
	b	3.1	5.2	5.1	8.0		

TABLE II

LEACHING OF TANNING MATERIALS (CRUSHED) WITH COLD WATER

a = % water solubles : b = % of 'a' on total leachables

	a	23.8	7.1	3.5	11.9	11.1	9.5
I							
	b	47.6	31.0	14.0	34.0		
	a	10.0	5.9	3.7	5.0	5.4	5.6
II							
	b	20.0	25.6	15.4	14.3		
	a	5.5	3.4	2.4	3.4	3.4	3.7
III							
	b	11.0	14.0	10.0	9.7		
	a	2.5	0.9	1.5	1.4	2.0	1.6
IV							
	b	5.0	3.8	6.4	4.0		
	a	2.2	0.9	1.3	1.3	1.2	1.6
V							
	b	4.8	3.8	5.5	3.8		
	a	1.3	0.8	1.5	1.2	1.3	1.5
VI							
	b	3.0	3.5	6.3	3.4		

TABLE III

ANALYSIS OF SPENT TAN MATERIALS

a = water solubles, b = % of "a" on total leachables

	Myrob		Babul		Goran		Wattle		Babul + Myrob 3 : 1		Goran Myrob 2 : 1	
	A	B	A	B	A	B	A	B	A	B	A	B
Water solubles (a)	3.0	2.6	9.4	4.0	12.0	10.1	20.9	9.5	14.3	7.6	16.8	10.2
Water solubles as a % of total solubles (b)	6.7	5.8	40.8	17.5	50.1	42.1	59.8	27.2				
Tans %	1.4	0.7	4.6	1.6	8.8	5.0	15.1	4.6	10.5	5.0	11.3	7.0
Non-tans %	1.6	1.9	4.8	2.6	3.2	5.1	5.8	4.9	3.8	2.6	5.5	3.2

A = Commercial samples: B = Crushed samples

TABLE IV

LEACHING OF CRUSHED MYROB AND BABUL AT 10°C

a = % water solubles, b = % of "a" on total leachables

Material	Leach No. I	II	III	IV	V	VI	VII	VIII	IX	Spent material TS.	Tans	Non tans
MYROB a	10.5	5.4	4.8	3.7	2.2	1.9	1.4	1.1	0.9	18.0	12.5	5.5
b	21.0	10.8	9.6	7.4	4.4	3.8	2.8	2.2	1.8	36.0	—	—
BABUL a	3.0	1.4	1.0	0.8	0.6	0.5	0.3	0.2	0.1	14.0	8.7	5.3
b	13.6	6.4	4.6	3.6	2.7	2.3	1.4	0.9	0.4	63.0	—	—